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FTIR STUDIES REVEAL THAT SILICON-CONTAINING LASER-INDUCED  
DESORPTION PRODUCTS ARE SURFACE REACTION INTERMEDIATES

P.Gupta, A.C. Dillon, P.A. Coon and S.M. George

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**FTIR Studies Reveal that Silicon-Containing Laser-Induced Desorption  
Products are Surface Reaction Intermediates**

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**Abstract**

Silicon-containing laser-induced desorption (LID) products such as SiOH and SiNH<sub>2</sub> have been observed from Si(111) 7x7 surfaces exposed to H<sub>2</sub>O and NH<sub>3</sub>. Assuming that the LID species were derived from surface reaction intermediates, these LID products were employed to examine the thermal stability of the SiOH and SiNH<sub>2</sub> surface species. Fourier transform infrared (FTIR) transmission spectroscopy was recently utilized to monitor the decomposition of SiOH and SiNH<sub>2</sub> surface species following the dissociative adsorption of H<sub>2</sub>O and NH<sub>3</sub> on porous silicon surfaces. The FTIR results on porous silicon surfaces were in excellent agreement with the previous LID studies on Si(111) 7 X 7. The correspondence between the FTIR and LID investigations indicates that silicon-containing LID products are derived from silicon surface reaction intermediates.



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## I. Introduction

Laser-induced desorption (LID) has recently been developed as a time-dependent probe of silicon surface processes. LID studies have monitored the desorption kinetics of hydrogen on Si(111) 7x7 (1) and Si(100) 2 X 1 (2) and the adsorption kinetics of molecular O<sub>2</sub> (3) and SiCl<sub>4</sub> (4) on Si(111) 7x7. LID investigations have also revealed that silicon-containing species can be desorbed from Si(111) 7x7 after exposure to H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>3</sub>OH and atomic hydrogen (5,6). Assuming that the silicon-containing species were derived from surface reaction intermediates, these LID products were employed to examine the thermal stability of SiOH and SiNH<sub>2</sub> species on Si(111) 7x7 after the dissociative adsorption of H<sub>2</sub>O (7) and NH<sub>3</sub> (6).

Although silicon-containing LID products may be directly derived from surface reaction intermediates, these species may also be generated by laser-driven processes or reactions in the gas phase. The correlation between silicon-containing LID products and surface species must be established before LID techniques can be used to study silicon surface reaction kinetics. This correlation can not be established with ordinary temperature-programmed desorption (TPD) studies because rapid laser-induced heating rates are required to desorb the silicon-containing species. The relationship between silicon-containing LID products and silicon surface reaction intermediates can be demonstrated using spectroscopic techniques.

Recently, transmission FTIR spectroscopy was utilized to determine the thermal stability of the SiOH and SiNH<sub>2</sub> silicon surface species following H<sub>2</sub>O (8) and NH<sub>3</sub> (9) exposure, respectively. These transmission FTIR studies were performed in UHV using high-surface-area porous silicon samples. In this letter, the FTIR results for the thermal stability of the SiOH and SiNH<sub>2</sub> surface species are compared with the corresponding LID studies on Si(111) 7x7. This comparison indicates that the silicon-containing LID products from Si(111) 7x7 are derived from silicon surface reaction intermediates.

## II. Experimental

Previous transmission FTIR studies have demonstrated that high-surface-area porous silicon can be used to monitor silicon surface chemistry (8-10). High-surface-area porous silicon surfaces are required for transmission FTIR spectroscopic studies because single-crystal samples do not have sufficient sensitivity given typical infrared cross sections of  $1 \times 10^{-18} \text{ cm}^2$  (10). The electrochemical techniques employed to prepare porous silicon have been described previously (10). Earlier studies have characterized the physical properties of porous silicon (12-14).

The surfaces of porous silicon are passivated with hydrogen after anodization. The infrared spectra of hydrogen on the anodized porous silicon surfaces is very similar to the infrared spectra of hydrogen on Si(100)  $2 \times 1$  (15). Initial studies on porous silicon have explored  $\text{H}_2$  desorption from monohydride and dihydride species (10). Desorption kinetics of  $\text{H}_2$  from these high surface area silicon surfaces were in agreement with  $\text{H}_2$  desorption kinetics obtained from isothermal LID studies on Si(111)  $7 \times 7$  (1,16).

In this study, hydrogen was first desorbed from the anodized porous silicon surfaces in UHV. The porous silicon surfaces were then exposed to  $\text{H}_2\text{O}$  and  $\text{NH}_3$  ( $\text{ND}_3$ ) at 300 K until a saturation coverage was obtained. Saturation exposures were typically performed at  $1 \times 10^{-5}$  Torr for 20 - 25 minutes. The porous silicon samples were then heated to progressively higher annealing temperatures for 60 seconds. After each annealing temperature, the FTIR spectra were recorded at 300 K.

FTIR studies were performed in a UHV chamber designed for *in-situ* transmission FTIR studies that has been described elsewhere (8-10). Compared with earlier descriptions (10), a sample introduction chamber and an isolation valve were added to facilitate a rapid recovery time after changing samples. A Nicolet 740 FTIR spectrometer was employed in these studies. The infrared beam passed through a pair of 0.5 inch thick CsI windows on the vacuum chamber. The O-ring seals on the CsI salt windows limited the typical base operating pressures in the FTIR chamber to  $1 \times 10^{-8}$  Torr.

For the LID studies, the Si(111) 7x7 were prepared and cleaned as described previously (1,6,7). The Si(111) 7x7 surfaces were then exposed to H<sub>2</sub>O and NH<sub>3</sub> (ND<sub>3</sub>) at 300 K until a saturation coverage was achieved. LID signals were subsequently obtained during linear temperature ramps of 2 K/sec for both H<sub>2</sub>O and ND<sub>3</sub> on Si(111) 7x7.

The experimental apparatus for the LID studies has been described previously (1). Briefly, the ultrahigh vacuum (UHV) chamber maintained a typical base pressure of  $4 \times 10^{-10}$  Torr. For surface analysis, the UHV chamber was equipped with a low-energy diffraction (LEED) spectrometer and a cylindrical mirror analyzer for Auger electron spectroscopy (AES). An Exrel C-50 quadrupole mass spectrometer was used for the laser-induced desorption (LID) experiments. The TEM-00 Q-switched Ruby laser employed in these LID studies had a temporal width of 100-120 nsec (FWHM) and a Gaussian spatial profile (1).

### III. Results

#### A. H<sub>2</sub>O Decomposition

The FTIR spectrum shown in Fig. 1 was obtained after a saturation H<sub>2</sub>O exposure on porous silicon at 300 K (8). This infrared spectrum shows the silicon hydride and silicon hydroxyl dissociation products following H<sub>2</sub>O adsorption, i.e.  $\text{H}_2\text{O} \rightarrow \text{SiH} + \text{SiOH}$ . The silicon hydride and silicon hydroxyl species were characterized by the Si-H stretching vibration at  $2090 \text{ cm}^{-1}$  and the SiO-H stretching vibration at  $3680 \text{ cm}^{-1}$ . These assignments are in agreement with previous EELS experiments of H<sub>2</sub>O on Si(111) 7x7 (17,18).

Figure 2 shows the change in the infrared spectrum of the SiO-H and Si-H stretching vibrations as a function of annealing temperature (8). Figure 2a displays the decrease in the absorbance of the SiO-H stretching vibration as the surface is annealed from 300 K to 640 K. Figure 2b displays the increase in the absorbance of the Si-H stretching vibration as the surface is annealed over the same temperature range.

Figure 3a displays the normalized integrated absorbance of the SiO-H and the Si-H stretching vibrations versus annealing temperature. The SiOH surface species has decomposed by

620K (8). Figure 3a also demonstrates that the SiH surface species increases by a factor of approximately 2 as the annealing temperature is increased from 300 K to 650 K. Above 650 K, the integrated absorbance for the Si-H stretching vibration decreases. This decrease is consistent with the thermal desorption of  $H_2$  from silicon surfaces (1,10,16,19).

The growth of surface silicon oxide has also been monitored by examining the absorbance of a Si-O-Si asymmetric stretch at  $950\text{ cm}^{-1}$  (8). The absorbance of the Si-O-Si stretch grows concurrently with the absorbance of the Si-H stretch. The increase of the integrated absorbance of both the Si-O-Si and Si-H stretching vibrations is caused by the decomposition of surface SiOH species to produce surface SiH and SiOSi species, i.e.  $SiOH \rightarrow SiH + SiOSi$ .

Following a saturation  $H_2O$  dose on Si(111) 7x7 (7), LID studies of  $H_2O$  decomposition on Si(111) 7x7 observed  $H_2$  and SiO thermal reaction products and a silicon-containing SiOH LID product at  $m=45$  amu. These results suggested that rapid LID heating rates were able to desorb surface reaction intermediates that could not be desorbed at slower heating rates (20,21). The temperature dependence of the LID signals for  $H_2$  and SiOH are shown in Fig. 3b after a saturation  $H_2O$  exposure on Si(111) 7x7 (7) at 110K.

Figure 3b reveals that the SiOH LID signal decreases progressively between 400 and 600 K. These SiOH LID results are in close agreement with the SiOH FTIR results shown in Fig. 3a. Fig. 3b also shows a progressive rise in the  $H_2$  LID signal with surface temperature. Separate LID experiments with hydrogen on Si(111) 7x7 indicated that this behaviour results primarily because of the temperature dependence of the LID signals (22,23). The decrease of the  $H_2$  LID signal at 800 K is consistent with the thermal desorption of  $H_2$  from Si(111) 7x7 (1,16,19).

## B. $NH_3$ Decomposition

Figure 4 displays the FTIR spectra after a saturation dose of  $NH_3$  on porous silicon at 300 K. The infrared features at  $1534\text{ cm}^{-1}$  and  $2077\text{ cm}^{-1}$  are assigned to the SiN- $H_2$  scissors mode and the Si-H stretching vibration, respectively (9). The FTIR spectra suggests that  $NH_3$  dissociative chemisorption on silicon surfaces occurs as  $NH_3 \rightarrow SiH + SiNH_2$ . These assignments

are in agreement with previous EELS studies of  $\text{NH}_3$  on  $\text{Si}(111) 7\times 7$  (24) and gas-phase infrared studies of substituted aminosilanes,  $\text{R}_3\text{SiNH}_2$  (25).

Figure 5 displays the change in the infrared spectrum of the  $\text{SiN-H}_2$  scissors mode and the Si-H stretching vibration as a function of annealing temperature (9). Figure 5a shows the decrease in the absorbance of the  $\text{SiN-H}_2$  scissors mode as the surface is annealed from 300 K to 680K. Figure 5b shows a broadening and increase in the absorbance of the Si-H stretching vibration as the surface is annealed in the same temperature range.

Figure 6a displays the normalized integrated absorbance of the  $\text{SiN-D}_2$  scissors mode and the Si-D stretching vibration versus annealing temperature (9). The integrated absorbance of the  $\text{SiN-D}_2$  scissors mode indicates that the  $\text{SiNH}_2$  surface species has decomposed by 700 K.  $\text{ND}_3$  was employed in Fig. 6 because a small SiO contamination interfered with the  $\text{SiNH}_2$  LID signal at  $m=44$  amu and prevented an accurate comparison of FTIR and LID results. The increase of the integrated absorbance of the Si-D stretching vibration is attributed to the decomposition of  $\text{SiND}_2$  species to produce SiD species, i.e.  $\text{SiND}_2 \rightarrow 2\text{SiD} + \text{Si}_3\text{N}$ . Above 650K, the decrease of the absorbance of the Si-D stretching vibration is caused by the desorption of  $\text{D}_2$  from the silicon surface (1, 10, 16, 19).

A variety of LID signals were observed from the  $\text{Si}(111) 7\times 7$  surface following a saturation  $\text{NH}_3$  exposure at 110K (6). Besides a large  $\text{H}_2$  LID signal,  $\text{SiNH}_2$  and  $\text{SiNH}$  LID signals were observed at  $m=44$  and  $m=43$ . These LID signals were used to monitor the thermal stability of hydrogen and  $\text{SiNH}_2$  species on the  $\text{Si}(111) 7\times 7$  surface in temperature-programmed LID experiments (6).

The temperature dependence of the LID signals for  $\text{D}_2$  and  $\text{SiND}_2$  is shown in Fig. 6b. The  $\text{SiND}_2$  LID signal decreased slowly between 400 and 700 K (6). These  $\text{SiND}_2$  LID results are in very good agreement with the  $\text{SiND}_2$  FTIR results shown in Fig. 6a. The  $\text{D}_2$  LID signal increases with surface temperature until  $\text{D}_2$  desorbs from the  $\text{Si}(111) 7\times 7$  surface at 800 K (1).



## IV. Discussion

LID and FTIR techniques are useful probes of silicon surface chemistry. LID is easily applied to single-crystal surfaces, but must observe products after they have desorbed from the surface. Transmission FTIR can observe surface species, but must be applied to high surface area samples for sufficient sensitivity. The association between silicon-containing LID species and surface reaction intermediates was a suggestion from the LID studies (5-7). This comparison of LID and FTIR results for  $\text{H}_2\text{O}$  and  $\text{NH}_3$  decomposition on Si(111) 7x7 and porous silicon surfaces was performed to test this hypothesis.

Previous EELS studies of  $\text{H}_2\text{O}$  absorption on Si(111) 7x7 surfaces (17,18) and reflectance infrared studies of water on Si (100) 2 X 1 (26) surfaces have observed SiO-H and Si-H stretching modes in agreement with Fig. 1. The dissociative adsorption of  $\text{H}_2\text{O}$  to produce SiH and SiOH on silicon surfaces has been fairly well established (8). The temperature-dependent decomposition of SiOH species and growth of SiH species monitored in Fig. 3a is also consistent with the reaction  $\text{SiOH} \rightarrow \text{SiH} + \text{SiOSi}$ . In particular, the twofold increase of the absorbance of the Si-H stretching vibration argues for an overall reaction of  $\text{SiH} + \text{SiOH} \rightarrow 2 \text{SiH} + \text{SiOSi}$ .

The correlation is excellent between the integrated absorbance of the SiO-H stretching vibration and the SiOH LID products versus temperature shown in Figs. 3a and 3b. If the laser was dictating the reaction products or if reactions in the gas phase were producing the silicon-containing LID products, this correspondence between the temperature dependence of the SiOH LID signal and the SiO-H infrared absorbance would not be expected. This correlation argues that the SiOH LID products from Si(111) 7x7 are derived from SiOH silicon surface species.

The dissociative adsorption of  $\text{NH}_3$  ( $\text{ND}_3$ ) to produce SiH and  $\text{SiNH}_2$  on silicon surfaces has been suggested by several studies (6, 9). In agreement with Fig. 4, previous EELS studies of  $\text{NH}_3$  and  $\text{ND}_3$  adsorption on Si(111) 7x7 have observed the SiN-H<sub>2</sub> (SiN-D<sub>2</sub>) scissors mode and the SiN-H<sub>2</sub> (SiND<sub>2</sub>) and Si-H stretching modes (24). The temperature-dependent decomposition of the  $\text{SiNH}_2$  species and growth of the SiH species monitored in Fig. 5 also suggests the

conversion of  $\text{SiNH}_2$  species to surface hydrogen species. Instead of the threefold increase expected if  $\text{SiH} + \text{SiNH}_2 \rightarrow 3 \text{SiH} + \text{Si}_3\text{N}$ , the absorbance of the Si-H stretching vibration increases approximately twofold. The recombinative thermal desorption of  $\text{NH}_3$  may explain this smaller increase (27).

The correlation is extremely good between the integrated absorbance of the  $\text{SiN-D}_2$  scissors mode and the  $\text{SiND}_2$  LID signal displayed in Figs. 6a and 6b. Both the integrated absorbance of the  $\text{SiN-D}_2$  scissors mode and the  $\text{SiND}_2$  LID products decrease between 450 -700 K. Very similar results are observed when comparing the temperature dependence of the integrated absorbance of the  $\text{SiN-H}_2$  scissors mode and the  $\text{SiND}_2$  LID signal (6). The close correspondence between the LID and FTIR results shown in Fig. 6 argues that the LID  $\text{SiNH}_2$  products are derived from  $\text{SiNH}_2$  surface species.

These FTIR results add to the accumulating evidence that rapid laser heating rates of  $10^{10}$  - $10^{11}$  K/sec can induce the desorption of many surface reaction species that normally would react at slower heating rates (20,21). For example, in addition to  $\text{SiOH}$  and  $\text{SiNH}_2$  LID products from  $\text{H}_2\text{O}$  and  $\text{NH}_3$  adsorbed on  $\text{Si}(111) 7 \times 7$ ,  $\text{SiOCH}_3$  is also observed from  $\text{CH}_3\text{OH}/\text{Si}(111) 7 \times 7$  (5). Likewise, at higher hydrogen coverages when the  $\beta_2 \text{H}_2$  -TPD peak corresponding to dihydride surface species is present (1, 10),  $\text{SiH}_x$  is detected as a LID product from  $\text{Si}(111) 7 \times 7$  (5).

On metal surfaces, there are numerous examples of LID products that have been observed that would have reacted at slower heating rates. For example,  $\text{CH}_3\text{OH}$  has been observed in the LID yield from  $\text{CH}_3\text{OH}/\text{Ni}(100)$  (28, 29) and  $\text{CH}_3\text{OH}/\text{Ru}(001)$  (30, 31). Likewise,  $\text{C}_2\text{H}_4$  has been detected as an LID product from  $\text{C}_2\text{H}_4$  adsorbed on  $\text{Ni}(100)$  (20) and  $\text{Pt}(111)$  (32).

The appearance of these LID products at rapid laser heating rates can be explained by the competition between desorption and reaction pathways (20, 21). In particular, many adsorbed reactants have desorption and reaction kinetics where the preexponential and activation barrier for desorption are both larger than the preexponential and activation barrier for reaction. In this case,

the rapid heating rates typically used in LID experiments will generally change the yield from reaction-dominated at slow heating rate to desorption-dominated at rapid heating rate (20,21). Inefficient thermal coupling between the surface and the reactants may also enhance the desorption pathway (33,34).

The ability to desorb surface reaction intermediates is extremely valuable for surface kinetic studies. In addition to the decomposition of SiOH (7) and SiNH<sub>2</sub> (6) on Si(111) 7x7, methanol decomposition on Ni(100) (28, 29) and Ru(001) (30, 31), ethylene decomposition on Ni(100) (20) and Pt(111) (32) and cyclohexane decomposition on Pt(111) (35) have all been studied using LID techniques. Because there is an excellent correlation between the silicon-containing LID products and surface reaction intermediates, these silicon-containing species should have general utility as a probe of reaction intermediates on silicon surfaces.

## V. Conclusions

Silicon-containing laser induced desorption (LID) products such as SiOH and SiNH<sub>2</sub> have been observed from Si(111) 7x7 surfaces exposed to H<sub>2</sub>O and NH<sub>3</sub>. Assuming that the silicon-containing LID species were derived from surface reaction intermediates, these LID products were used to examine the thermal stability of the SiOH and SiNH<sub>2</sub> surface species. At saturation coverage, the SiOH and SiNH<sub>2</sub> surface species were both observed to decompose slowly over a wide temperature range from 400 K - 600 K.

In complementary studies, Fourier transform infrared (FTIR) transmission spectroscopy was used to monitor the decomposition of H<sub>2</sub>O and NH<sub>3</sub> on porous silicon surfaces. The FTIR spectra observed SiOH and SiNH<sub>2</sub> surface species following the dissociative adsorption of H<sub>2</sub>O and NH<sub>3</sub>. The FTIR results for the thermal stability of the SiOH and SiNH<sub>2</sub> surface species were in excellent agreement with the previous LID studies on Si(111) 7 X 7. The correspondence between the FTIR and LID investigations indicates that silicon-containing LID products are derived from silicon surface reaction intermediates.

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## Figure Captions

1. Infrared spectrum after a saturation  $\text{H}_2\text{O}$  exposure on porous silicon surfaces at 300K.
2. Infrared absorbance as a function of annealing temperature after a saturation  $\text{H}_2\text{O}$  exposure at 300 K for a) the SiO-H stretching vibration and b) the Si-H stretching vibration.
3. a) Integrated infrared absorbances of the SiO-H and Si-H stretching vibrations at  $3680\text{ cm}^{-1}$  and  $2090\text{ cm}^{-1}$ , respectively, versus annealing temperature after a saturation  $\text{H}_2\text{O}$  exposure on porous silicon surfaces at 300 K.  
b) LID signals for  $\text{H}_2$  and SiOH during a linear temperature ramp at 2 K/s following a saturation  $\text{H}_2\text{O}$  exposure on Si(111) 7x7 at 110 K.
4. Infrared spectrum after a saturation  $\text{NH}_3$  exposure on porous silicon surfaces at 300 K.
5. Infrared absorbances as a function of annealing temperature after a saturation  $\text{NH}_3$  exposure at 300 K for a) the SiN- $\text{H}_2$  scissors vibration and b) the Si-H stretching vibration.
6. a) Integrated infrared absorbances of the SiN- $\text{D}_2$  scissors and the SiD stretching vibrations at  $1534\text{ cm}^{-1}$  and  $2077\text{ cm}^{-1}$ , respectively, versus annealing temperature after a saturation  $\text{ND}_3$  on porous silicon surfaces at 300 K.  
b) LID signals for  $\text{D}_2$  and SiND<sub>2</sub> during a linear temperature ramp at 2 K/s following a saturation  $\text{ND}_3$  exposure on Si(111) 7x7 at 110 K.

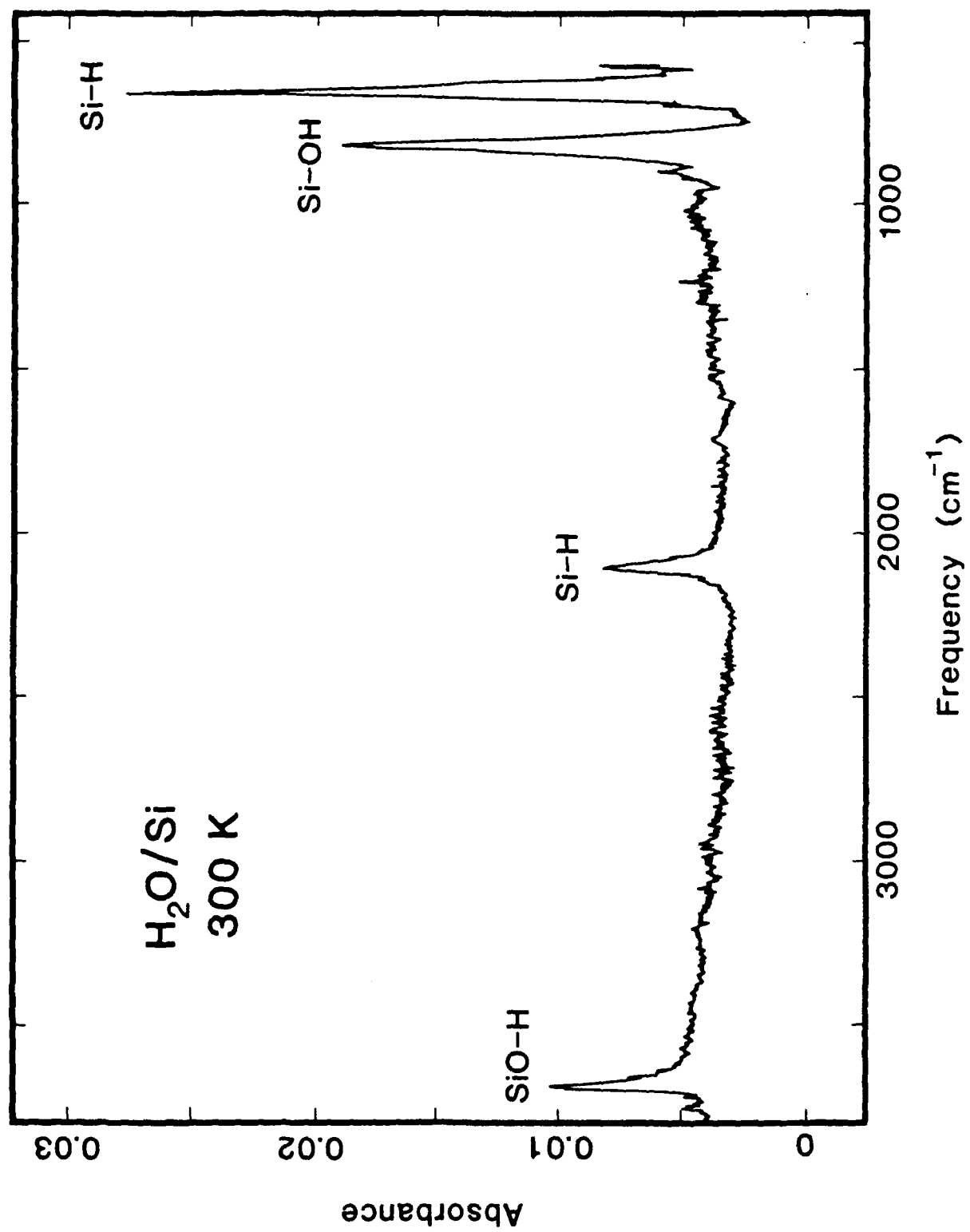


Figure 1



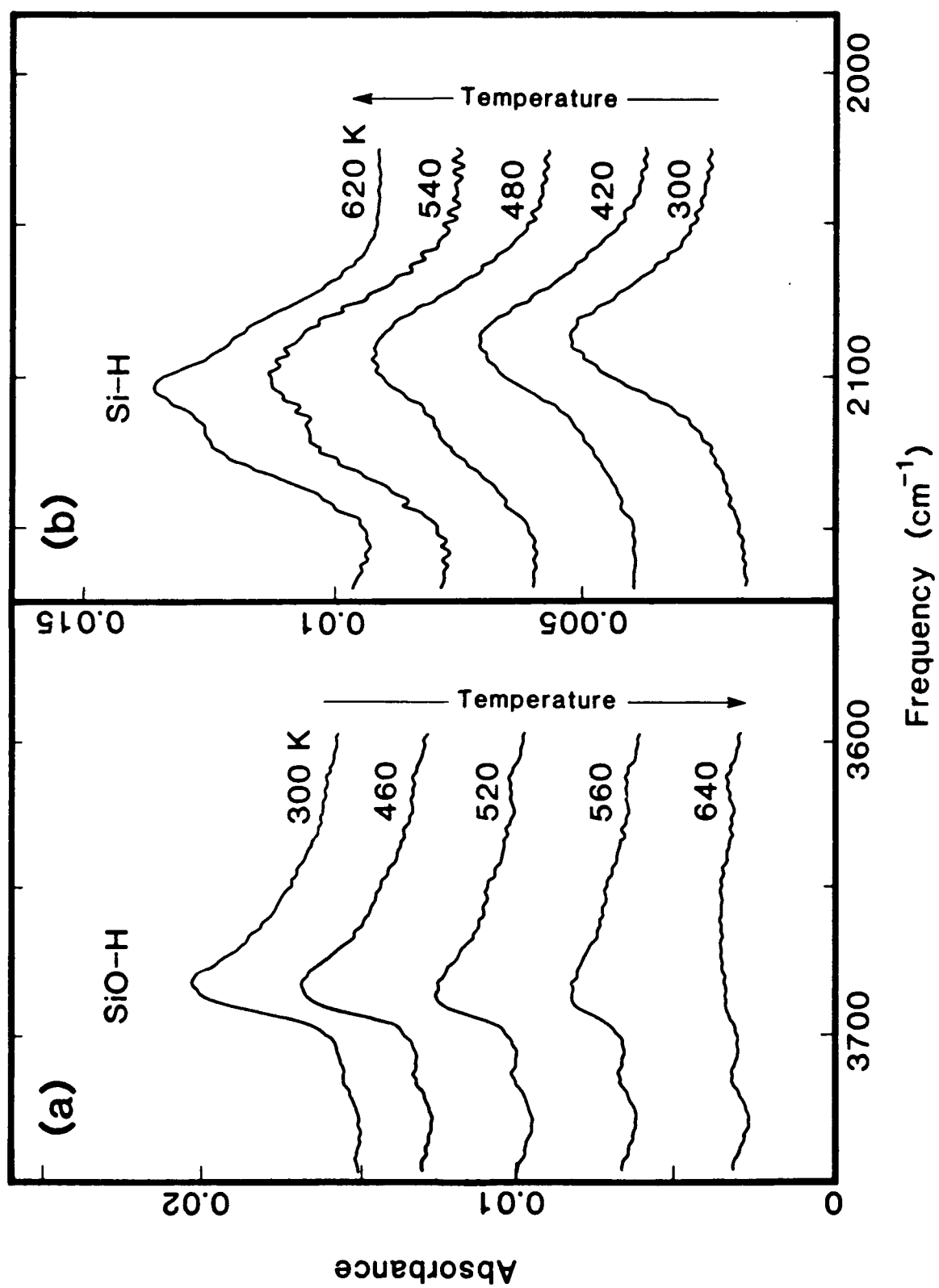


Figure 2

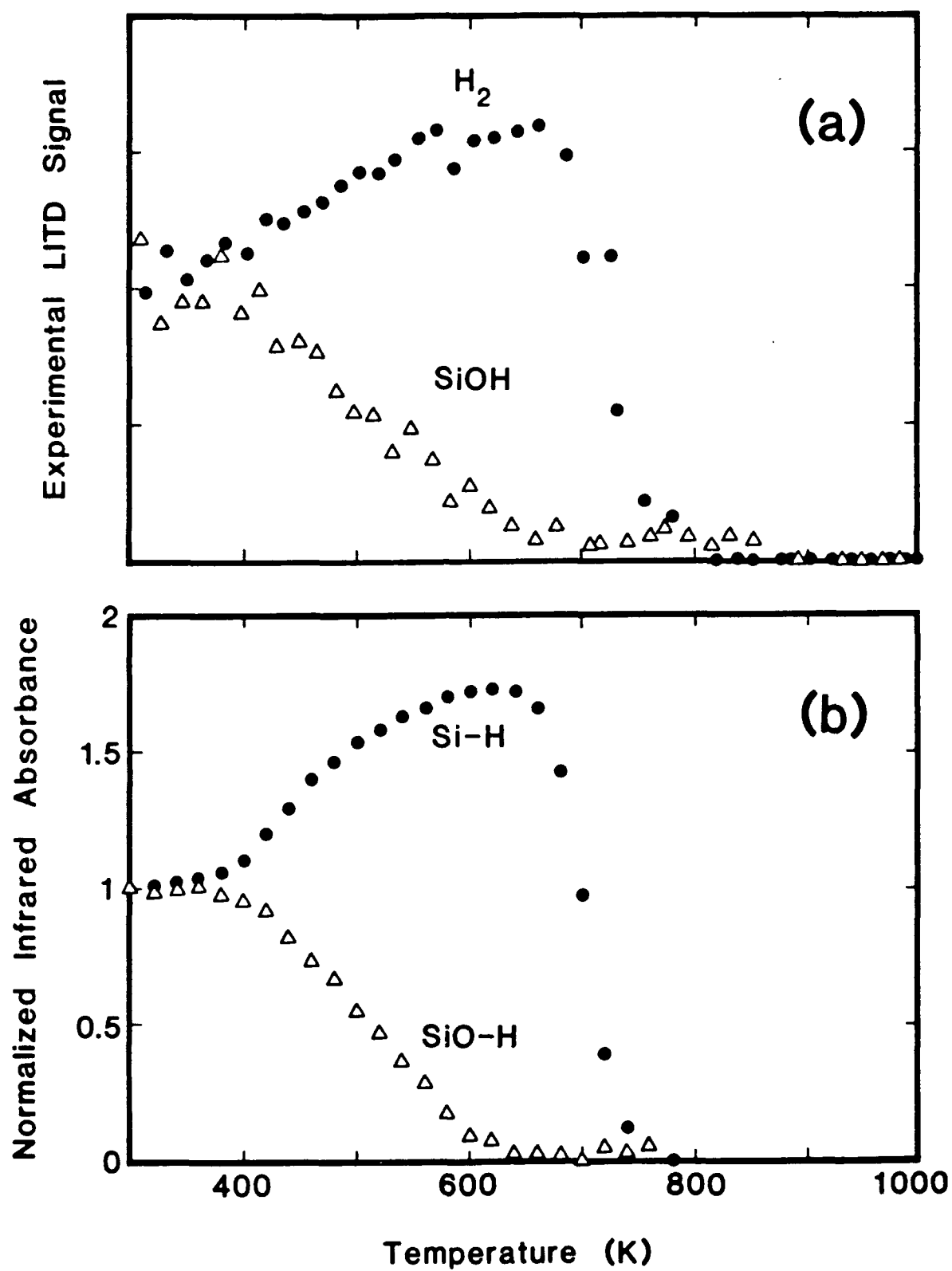


Figure 3

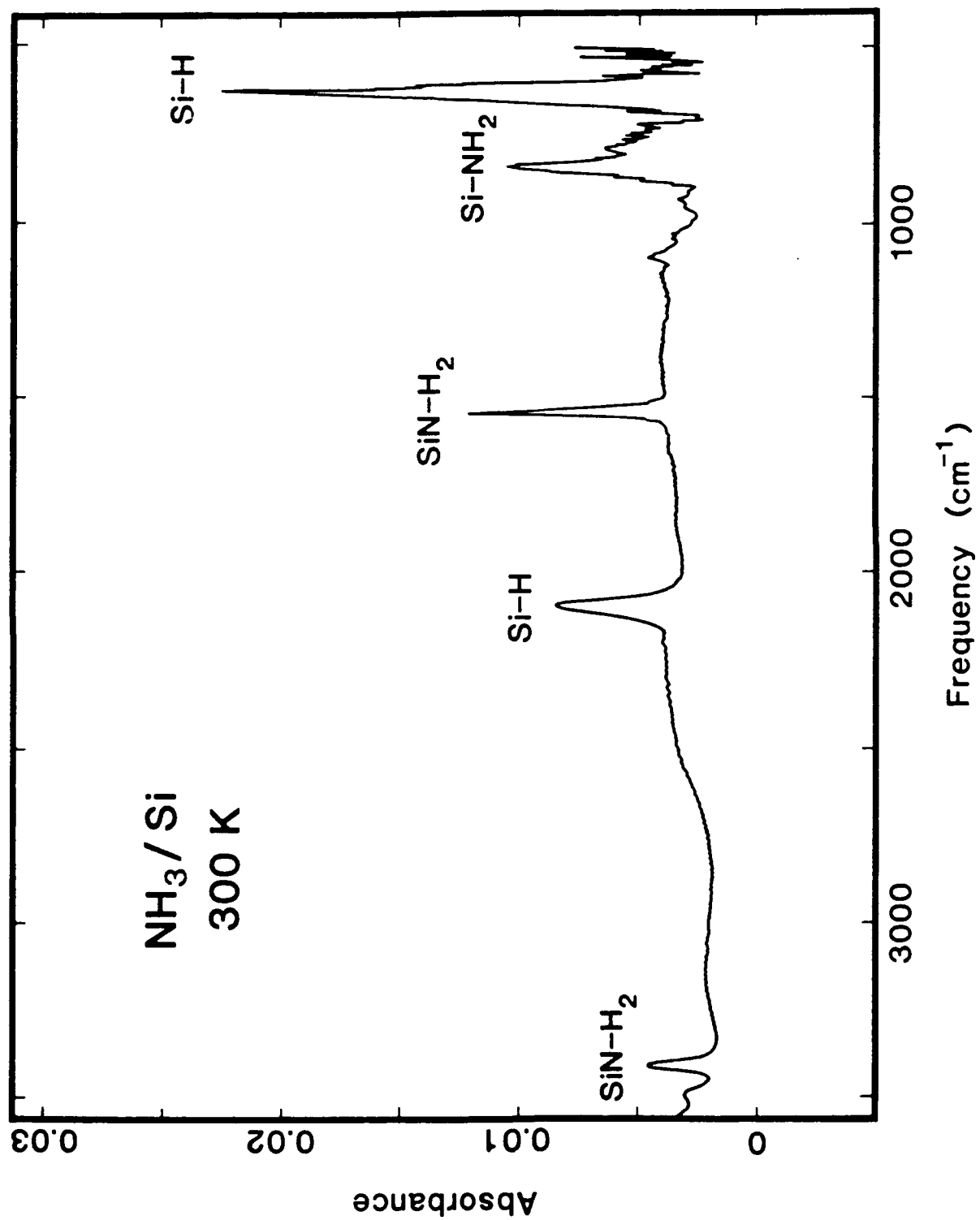


Figure 4

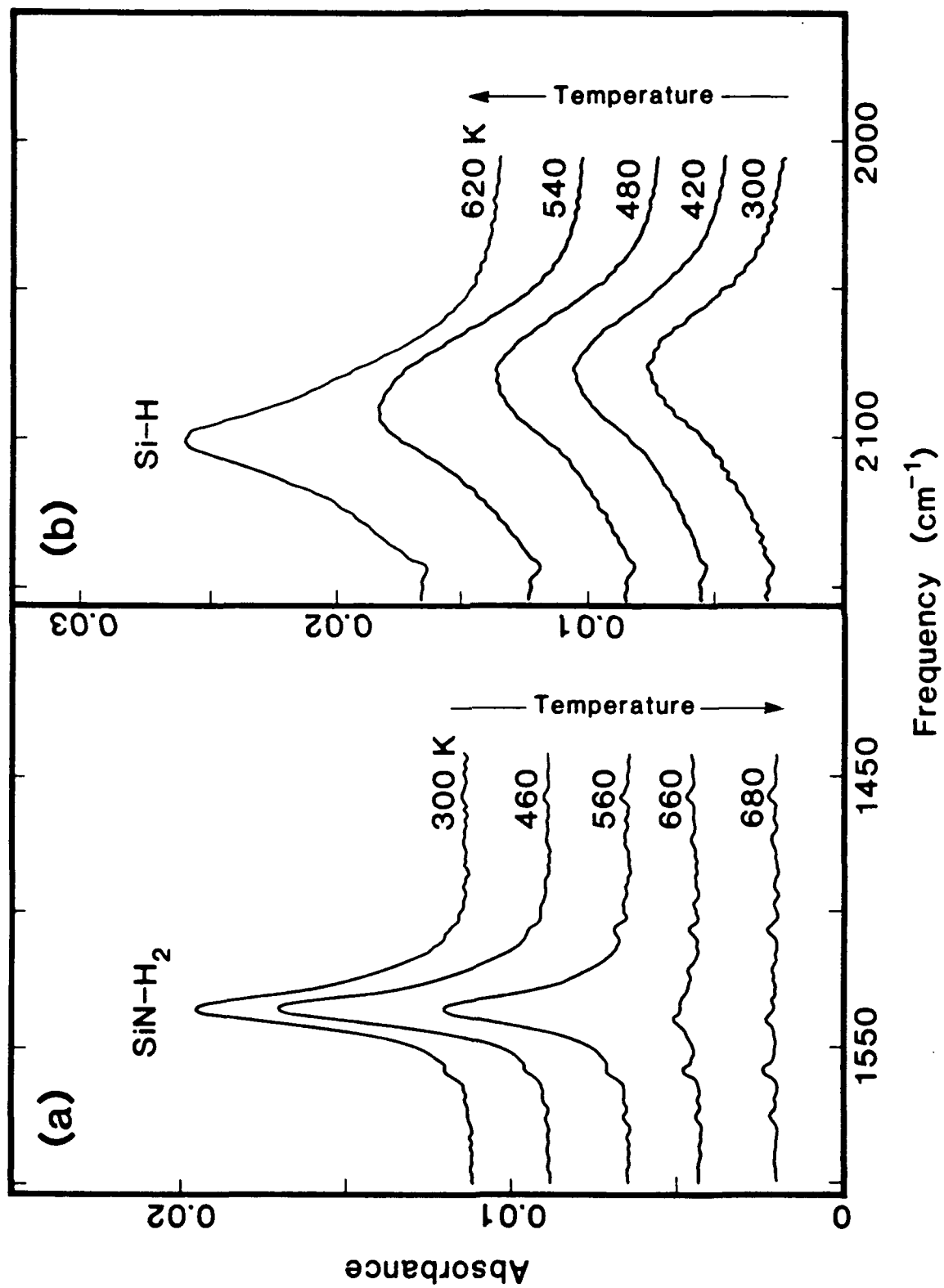


Figure 5

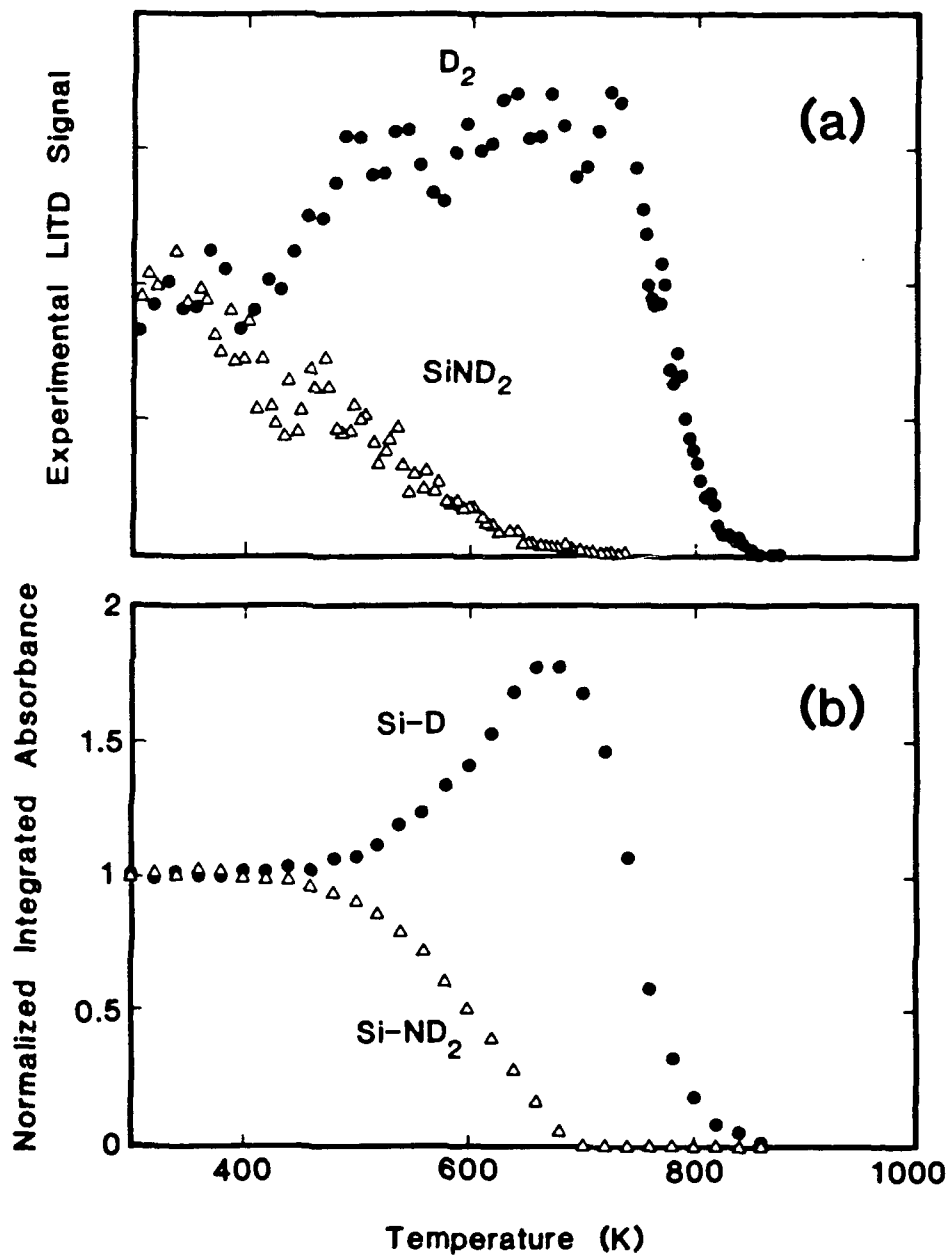


Figure 6